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Intramolecular evolution from a locally excited state to an excimer-like state in a multichromophoric dendrimer evidenced by a femtosecond fluorescence upconversion study

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Abstract

A time-resolved fluorescence upconversion study on a polyphenylene dendrimer with eight peryleneimide chromophores on the surface (**1**) and on a monochromophoric model compound (**2**) is reported. The time-dependent fluorescence spectra of the dendrimer show that the initial excitation is into a locally excited chromophore. They further indicate the existence of a decay channel that leads to excited state interaction between chromophores in one dendrimer which takes place on a 5 ps timescale. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Dendrimers are highly branched macromolecular systems whose structure can be defined on a molecular level [1,2] and as such have been attracting a lot of attention not only from the synthetic point of view [3], but also from the point of view of their physical and chemical properties [4–7].

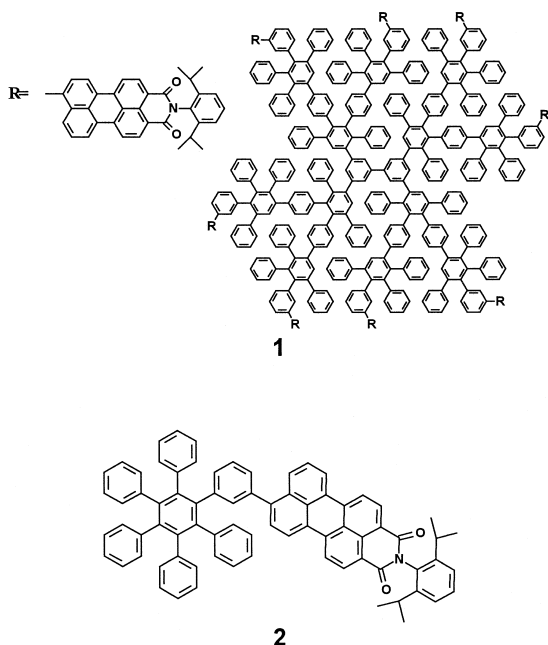
Within the research group, these molecules have been chosen for single-molecule spectroscopy [8,9] because they allow to combine topographic and optical observation on a single-molecule level. In order to understand the dynamics of single-molecule spectroscopy, it is essential to evaluate the photophysical

processes at the ensemble level. In the present contribution, a dendrimer with a polyphenylene core decorated with eight peryleneimide chromophores on the surface (**1**, Scheme 1) is compared to a model compound (**2**) in which a hexaphenylbenzene unit is attached to a peryleneimide. Furthermore, these dendrimers have relative shape persistence and through synthesis [10] one can control the number of the peryleneimide chromophores.

In a previous publication, the photophysical properties of **1**, studied using single-photon timing (SPT) and femtosecond transient absorption, were reported ¹. The hydrodynamic volume calculated

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¹ The values of the quantum yield in this Letter were 0.65 for **1** and 0.82 for **2**, but they were remeasured using rhodamine 101 as a reference and these values should be corrected (see Ref. [11]).



Scheme 1. Molecular structure of dendrimer **1** and the model compound hexaphenylbenzene peryleneimide **2**.

from anisotropy decay measurements led to a value of 4 nm as a rigid rotor diameter for **1**. Based on steady-state spectroscopy information of the peryleneimide model compound **2**, the Förster radius for dipole–dipole energy transfer was calculated to be 2.5 nm. It is therefore very probable that in the dendrimer **1** two chromophores will be closer to each other than the Förster radius. The fluorescence decay of **2**, measured by SPT, was found to be mono-exponential with a decay time of 4.2 ns, while the fluorescence decay of **1** was found to be three-exponential with a long decay time of 7.6 ns. It was suggested that this longest decay component could be due to the excited state excimer-like interactions among neighboring peryleneimides. The observation of a 4 ps component in the transient absorption anisotropy measurements suggested the existence of an energy migration process.

In this Letter, fluorescence upconversion measurements of compounds **1** and **2** are reported, revealing a relaxation of the locally excited state to a state in which excitation is delocalized over several chromophores as in an excimer.

2. Experimental

The synthesis of the dendrimer (**1**) and the peryleneimide model compound (**2**) (Scheme 1) has been reported elsewhere [10]. Chloroform (Aldrich, spectro-grade) has been used as a solvent without further purification. The ground state spectra have been recorded on a spectrophotometer (Lambda 6, Perkin Elmer). A fluorometer (Spex) has been used for steady-state fluorescence measurements.

2.1. Fluorescence upconversion setup

A Nd:YVO₄ laser (Millennia, Spectra Physics) was used to pump a Ti:Sapphire laser (Tsunami, Spectra Physics). Its output seeds a regenerative amplifier (RGA) (Spitfire, Spectra Physics). The output of the amplifier (1 mJ, 100 fs, 800 nm) is split in two equal parts, one of which is used to pump an optical parametric generator/amplifier (OPA-800, Spectra Physics). The output wavelength of this was tripled by harmonic generation using two BBO crystals, and was focused onto the sample. The resulting fluorescence was collected and focused onto a 1 mm LBO crystal. The second part of the RGA output was sent into a variable delay and served as the optical gate for the upconversion of the fluorescence. The generated sum frequency light was then collimated and focused into the entrance slit of a 300 mm monochromator (300I, Acton Research). An UV-sensitive photomultiplier tube (R1527p, Hamamatsu) detected the signal. The electrical signal from the photomultiplier tube was gated by a boxcar averager (SR250, Stanford Research Systems) and phase sensitively detected by a lock-in amplifier (SR830, Stanford Research Systems).

To examine the population dynamics, the polarization plane of the excitation light was set to magic angle (55°) with respect to that of the gating pulse.

Decay curves were detected every 10 nm at wavelengths between 540 and 700 nm.

3. Results and discussion

The steady-state absorption and fluorescence spectra of **1** and **2** are shown in Fig. 1. The ground state absorption spectra of the two compounds are

very similar, minor differences are in the maximum of the spectrum that is structured in **2** and in the spectral bandwidth that is 140 cm^{-1} wider in **1**. The fluorescence spectra show more drastic differences, the spectrum of **2** has a maximum at 574 nm and a shoulder at 600 nm, while the spectrum of **1** is structureless and its maximum is shifted to the red by 1450 cm^{-1} . As reported previously, the fluorescence quantum yield decreases from 96% in **2** to 76% in **1** [11].

Upconversion measurements of the fluorescence decay were taken in three time windows of 7, 50 and 420 ps. Fig. 2 shows fluorescence decay curves of **1** which were detected at various wavelengths along with the corresponding fit curves. The excitation wavelength was 500 nm in all cases.

The instrument response function (IRF) was obtained by an upconversion measurement of the residual excitation light scattered from the sample and has a typical temporal width of 300 fs (full width at half maximum, FWHM). The Levenberg–Marquardt minimization algorithm of a commercial software package (Origin, Microcal) was used to fit the data by a sum of exponentials convoluted with the IRF. The data could successfully be fitted by a function comprised of three exponentials convoluted with the IRF, as judged by inspection of the residual plots and minimizing the χ^2 value.

The time-dependent fluorescence spectra cannot be constructed directly from the upconversion signal, because the spectral response of the setup, which is not flat, depends on the upconversion efficiency, the

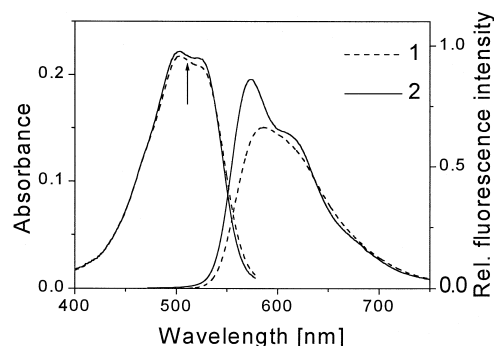


Fig. 1. Absorption and emission spectra of **1** (dashed) and **2** (solid) in CHCl_3 at room temperature. The arrow indicates the position of the excitation.

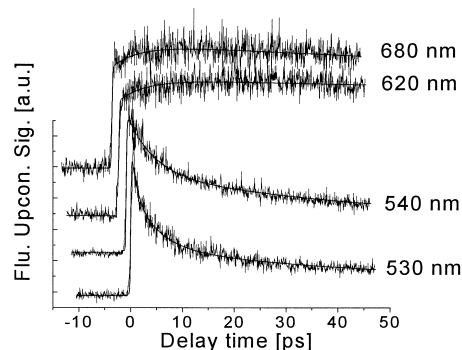


Fig. 2. Fluorescence decay curves of **1**. The excitation was at 500 nm, while the detection of the upconversion signal was made at 318.8, 322.4, 349.3 and 367.6 nm. These wavelengths correspond to the sum frequency of the 800 nm gate light with emission at 530, 540, 620 and 680 nm. The solid lines are the corresponding numerical fits.

photomultiplier, the monochromator and the reflecting optics. All these factors depend on the wavelength in a complex way. One method to overcome this problem is to assume that at large delay time, typically 30 ps, the fluorescence spectrum is similar to the steady-state spectrum. This approach is not suitable for **1** since the fluorescence decay is multi-exponential even on the nanosecond timescale [11]. Thus the steady-state spectrum should be compared to an integral over the complete decay trace. The longest measurement window possible with the upconversion is 420 ps. In order to extend the integration window behind this point, the fluorescence upconversion decay traces $f^{\text{UC}}(t; \lambda)$ were matched to the single-photon timing (SPT) decay traces $f^{\text{SPT}}(t; \lambda)$, which were reported previously [11,12], at $t = 400$ ps. This allows one to calculate the time integrals of the fluorescence intensity over the complete decay curves $f(t, \lambda)$, at each wavelength λ . The fluorescence quantum flux function (Φ), which takes into account the spectral response function of the instrument, is calculated by:

$$\Phi(t, \lambda) = \frac{f(t, \lambda)}{\int_0^\infty f(t, \lambda) dt} \frac{F(\lambda) q_f}{\int_0^\infty F(\lambda)} \quad (1)$$

here $f(t, \lambda)$ are the decay curves corrected by the IRF, $F(\lambda)$ is the steady-state fluorescence spectrum and q_f is the fluorescence quantum yield. The value $\Phi(t, \lambda) dt d\lambda$ is interpreted as the probability that a

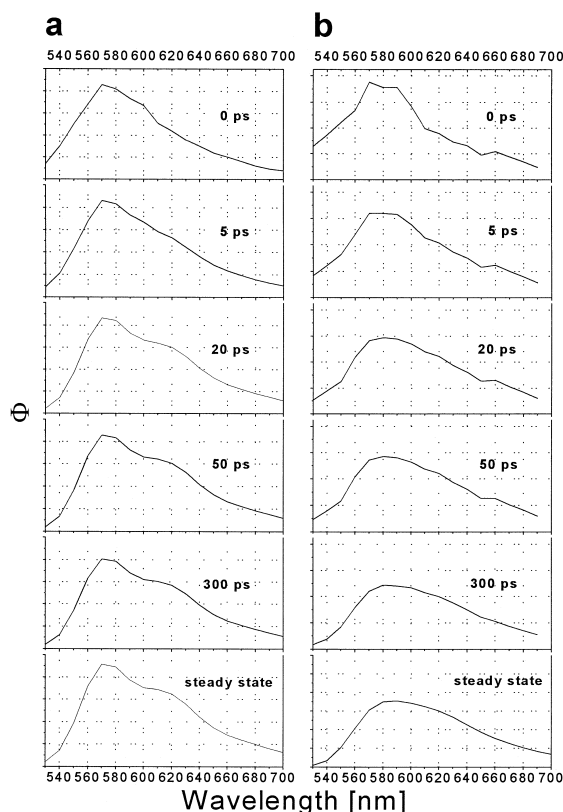


Fig. 3. Evolution of the fluorescence spectra in the first 300 ps. The excitation was made at 500 nm. (a) Time-dependent spectra of hexaphenyl peryleneimide **2**. (b) Time-dependent spectra of the dendrimer **1**. All spectra were normalized using the same factors.

photon whose wavelength is in the range $\lambda \rightarrow \lambda + d\lambda$ is emitted in the time interval $t \rightarrow t + dt$ following absorption of one photon. This function has a quantitative meaning and thus allows to compare between different compounds.

The fluorescence quantum flux function plotted versus the wavelength at fixed times is proportional to the time-dependent spectra. These spectra of **2** are shown in Fig. 3a. In the first picoseconds, at 624 nm a rise of the $0 \rightarrow 1$ vibronic band is observed. These spectral changes can be attributed to relaxation of vibrationally hot excited molecules [13–15] from which emission to the vibrationally excited ground state is forbidden. However, at times longer than 20 ps, no structural changes are observed. This corresponds to the single exponential decay on the nanosecond timescale reported previously [11].

The time-dependent spectra of **1** (Fig. 3b) are more complex. Immediately after the excitation, the spectrum is similar to the spectrum of **2** at $t = 0$ with a structure that is typical for the isolated chromophore. However, in the following 20 ps the spectrum loses its vibrational structure and becomes similar to the steady-state spectrum of **1**. These results suggest that upon excitation of **1** a locally excited state is obtained. At longer times the emission spectrum of **1**, contrary to that of the model compound, becomes structureless.

The fluorescence quantum flux functions $\Phi(t, \lambda)$ of the dendrimer **1** and the model compound **2** could be fitted by sets of exponentials decay function of the form

$$\Phi^{\text{fit}}(t, \lambda) = \sum_i \alpha_i(\lambda) \exp(-t/\tau_i). \quad (2)$$

With a wavelength-independent set of decay times and a sum of three exponentials, the data obtained for the dendrimer **1** could be fitted using values of the decay times of 5 ps, 200 ps and a few nanoseconds. The latter could not be exactly determined using upconversion in view of the window limitation to 420 ps. The data obtained for the model compound **2** could be fitted using only two decay times: one of 5 ps and one in the nanosecond timescale.

To get information on the evolution of the emissive states, the amplitudes associated with the 5 ps time constant ($\alpha_{5\text{ps}}$ in Eq. (2)) are plotted as a function of the wavelengths (Fig. 4). In the model

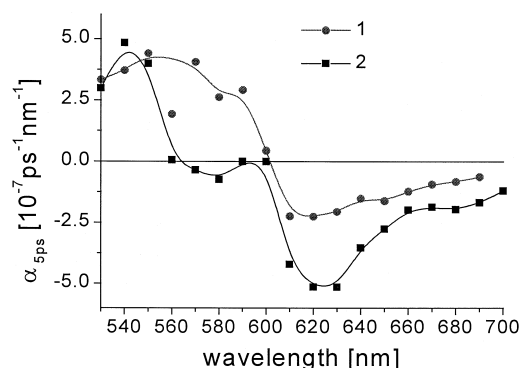


Fig. 4. Amplitudes of the 5 ps component in the fluorescence quantum flux function of the dendrimer **1** and the model compound **2** as function of wavelength, as resulting from the data analysis.

compound **2**, these amplitudes are positive at the shorter wavelength domain, they become almost zero at wavelengths between 560 and 600 nm and then strongly negative at wavelengths between 600 and 700 nm, which correspond to the maximum of the 0 → 1 vibrational band of the fluorescence at 625 nm. This behavior of the amplitude spectrum is typical for relaxation processes and may be attributed to a vibrational relaxation of the excited state. In the dendrimer **1** the amplitudes of the 5 ps component are also positive at the shorter wavelength domain, but they are still positive at the wavelengths between 560 and 600 nm and then become negative at wavelengths between 600 and 700 nm. The similarity between the amplitudes of the dendrimers and the model compound in the wavelength domain between 530 and 550 nm further support the assumption that excitation of the dendrimer is made into a locally excited chromophore. The high positive amplitudes in the wavelength domain between 560 and 600 nm are associated with the loss of the vibronic structure in the fluorescence spectrum of **1**, and indicate that a different species is formed. The negative amplitudes at the longer wavelength domain of **1** together with the spectral change indicate, beside the vibrational relaxation, the formation of an emitting species. The lower absolute value of these amplitudes in the dendrimer **1** in comparison to **2**, can be explained by a lower quantum yield for fluorescence and a longer lifetime of this species in the dendrimer. This is in agreement with the lower fluorescence quantum yield (0.76) in the dendrimer relative to the model compound (0.96) and the long (7 ns) decay time, which were previously reported [11]. This emitting species may be an excited state complex between two or more chromophores, which contain the locally excited chromophore or to which the excitation energy is transferred. An excited state complex between chromophores is suggested rather than a complex between a chromophore and the core because the previously mentioned long decay time (7 ns) is found for the model at high concentrations ($> 10^{-2}$ M) [12]. Further evidence for the excimer like state can be found by analyzing the time-resolved fluorescence traces of the first generation of the dendrimer, consisting of a similar core but containing only four chromophores. The contribution of the long-lived decay in the first generation of the

dendrimer is much smaller [12] than in dendrimer **1**, again indicating a chromophore/chromophore interaction rather than a chromophore/core interaction. Moreover, the picosecond time-resolved fluorescence measurements show that the 200 ps component also contributes to the formation of the excimer like state [12].

Furthermore, the association of the 5 ps component in **1** with the trapping of the energy in an excited state complex is in agreement with the observation of the 4 ps component in the transient absorption anisotropy decay [11], as this process would lead to a change in orientation of the transition dipole moment.

4. Conclusions

The comparative time-resolved fluorescence up-conversion study of a dendrimer containing eight peryleneimide chromophores on the surface of a polyphenylene core **1** and its peryleneimide model compound **2** reveals a slow vibrational relaxation for both **1** and **2** and an additional excited state process which was observed for **1** only.

The time dependent fluorescence spectra of the dendrimer show that the initial excitation is made into a locally excited chromophore with a fluorescence spectrum similar to that of the model compound. The comparison between the amplitudes of the fitted pre-exponential fluorescence quantum flux functions of the dendrimer **1** and the model compound **2** further suggests the evolution to another excited species occurring in **1**. In this species the excitation energy migrates to or is delocalized in an excimer-like state between two or more chromophores.

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